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THE EFFECT OF COMPOSITION ON THE PROPERTIES OF HYDRONIUM ZIRPSIOS

by

A.K. Kuriakose*, A. Ahmad*, J.D. Canaday* and T.A. Wheat**

ABSTRACT

The preparation and characterization of hydronium zirpsios (hydrogen-ion conducting Nasicons with the general formula: $Na(H_3O)_xZr_2Si_xP_{(3-x)}O_{12}$) as a function of their x values (between x=0.5 and x=2.0) are reported. Thermogravimetric analysis of these materials shows that their thermal stability increases with a decrease in the x value. Although thermal stability is highly desirable for these products, the fabrication of membranes has been successful only using compositions with $x \geq 1.5$. Currently, the composition with x = 1.5 appears to be the most promising, based on physicochemical properties and hydrogen-ion conductivity.

Keywords: hydrogen conductors, bonded hydronium zirpsios, hydronium Nasicons

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EFFET DE LA COMPOSITION SUR LES PROPRIÉTÉS DE L'HYDRONIUM ZIRPSIOS

par

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RÉSUMÉ

Le présent rapport décrit la préparation et la caractérisation de l'hydronium zirpsios [Nasicons conducteurs d'hydrogène-ion dont la formule générale est la suivante: $Na(H_3O)_xZr_2si_xP_{(3-x)}O_{12}$] en tant que fonction de leurs valeurs x (entre x=0,5 et x=2,0). Les résultats de l'analyse thermogravimétrique de ces matériaux indiquent que leur stabilité thermique augmente avec une diminution de la valeur x. Bien que l'obtention d'une stabilité thermique soit très souhaitable pour ces matériaux, la fabrication de membranes n'a été réussie qu'avec l'emploi de compositions où $x \geq 1,5$. Actuellement, il semble que la composition la plus prometteuse est celle dont la valeur x = 1,5 en raison des propriétés physicochimiques et de la conductivité hydrogène-ion.

Mots-clés: conducteurs de l'hydrogène, hydronium zirpsios lié, hydronium Nasicons.

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INTRODUCTION

The technological applications of hydrogen-ion conducting solid electrolytes are many, if a highly conductive material which is stable to at least 100°C may be developed. The major potential applications involve the use of these as hydrogen conducting membranes in devices such as hydrogen-air fuel cells, hydrogen or hydrogen isotope separators, water/steam electrolysers, and hydrogen detectors. Most of the known hydrogen ion conductors are, however, either unstable at temperatures slightly above room temperature or are extremely poor in their ionic conductivity. Two attractive candidates in this class of materials are hydronium beta"-alumina and hydronium zirpsios. These compounds have the required stability and ionic conductivity in the single crystal form, but the fabrication of membranes of sufficient size using these materials has been difficult. At CANMET a new technique has been developed to overcome this problem by bonding the finely divided powder of the material using a hydrogen conducting inorganic compound (1). Hydronium zirpsio membranes fabricated by this technique were found to be superior to the hydronium beta"-alumina with respect to their ionic conductivity. Because the properties of sodium zirpsios vary with their composition, the present investigation was undertaken in order to determine the optimum hydronium zirpsio composition, if any, by analogy, that might provide the best hydrogen ion conductivity and other properties. This report describes the behaviour of hydronium zirpsios as a function of their composition (x-value in the general formula for hydronium zirpsios represented by : $Na(H_3O)_xZr_2Si_xP_{(3-x)}O_{12}$) in the bonding process and in other properties such as thermal stability and ionic conductivity.

EXPERIMENTAL

Materials: Sodium carbonate and ammonium dihydrogen phosphate (both reagent grade), silica fume (Cabosil M-5), zirconium hydroxide slurry (prepared in the laboratory by the hydrolysis of zirconyl chloride),

hydrochloric acid (C.P.) and phosphoric acid (C.P.) were the chemicals used in the synthesis and fabrication of the products.

Equipment: Buchi mini spray-dryer, furnaces, reflux condenser and flask, press and dies, instruments for measurement of ionic conductivity.

Procedure: Precursor powders for sodium zirpsios were first prepared by spray-drying slurries made from calculated amounts of sodium carbonate, ammonium dihydrogen phosphate, silica fume and zirconium hydroxide. The resulting powders were calcined at about 1250°C to synthesize the sodium zirpsio powders. These powders were then boiled with 0.1N hydrochloric acid under reflux to convert the sodium zirpsios into the hydronium form. Taking Nazirpsio at x = 2 as an example, these various processes may be represented by the following chemical equations:

$$3Na_2CO_3+2NH_4H_2PO_4+4SiO_2+4Zr(OH)_4 \text{ --->} 2Na_3Zr_2Si_2PO_{12}+2NH_3+11H_2O+3CO_2$$

$$Na_3Zr_2Si_2PO_{12}+2HCl+2H_2O \text{ ---> } Na(H_3O)_2Zr_2Si_2PO_{12}+2NaCl$$

Sodium zirpsios of various compositions (x values ranging from 0.5 to 2.0 in the general formula $Na_{(1+x)}Zr_2Si_xP_{(3-x)}O_{12}$) were first synthesized. These were subsequently converted into the corresponding hydronium zirpsios in powder form and were then characterized by TGA (thermogravimetric analysis) and X-ray diffraction.

The hydronium zirpsio powders so obtained were bonded using phosphoric acid under pressure at a temperature of about 120°C into discs measuring about 2.5 cm in diameter and about 3 mm in thickness. Teflon spacers and liners were used to protect the metal moulds from the corrosive phosphoric acid during the fabrication of the discs. The bonded hydronium zirpsio discs were then evaluated by their physical characteristics and ionic conductivity.

Conductivity measurements (ac) were made on the hydronium zirpsio discs (~ 2.5 in diameter and ~3 mm in thickness) after application of platinum ink electrodes to both sides. A fully automated system consisting of a Solartron 1174 Impedence Analyser and a Solartron 1186 Electrochemical Interface connected to a Hewlett-Packard 9485 desk top computer via an IEEE-488 interface was used for these measurements. After drying the electrodes at 90°C for 2 h in air, conductivity data were obtained over the temperature range of 25 to 120°C in air, at approximately 25° intervals.

The temperature of the furnace in which the samples were held for measurement was controlled by a Leeds & Northrup Electromax V controller, and was monitored and recorded using an HP-3497A data acquisition system. Admittance plots were obtained by plotting Susceptance (B) vs. Conductance (G) as a function of the ac signal in the range of 10 Hz to 500 kHz. These plots were obtained during both heating and cooling cycles. The conductivity values were obtained by extrapolating the high frequency spur to zero susceptance.

RESULTS AND DISCUSSION

CONVERSION OF THE SODIUM ZIRPSIOS TO THE HYDRONIUM FORM

All the samples of sodium zirpsio underwent hydronium ion exchange in 6 to 12 h by boiling in 0.1N hydrochloric acid. The extent of the ion exchange was monitored by X-ray analysis of the product and also by the property of total decomposition of the hydronium compound when heated to about 800°C. Compounds with $x = 1.5$ and higher, on hydronium ion exchange, yielded products which decomposed to amorphous phases when heated to about 800°C. On the other hand, at $x = 1.0$ and 0.5, after the hydronium ion exchange, the products retained a certain level of crystallinity after heating to 800°C. Thus it appears that at very low x values, the loss of water from the samples is very low so that it does not totally disrupt the crystal structure of the material.

THE THERMAL STABILITY OF HYDRONIUM ZIRPSIOS

Thermogravimetric analysis (TGA) was used to determine the thermal stability of the hydronium zirpsios. In Fig. 1 and 2 are shown the TGA curves and the DTG (differential thermogravimetric) curves respectively for zirpsios of x values ranging from 0.5 to 2.0. All the samples begin to lose weight at about 125°C corresponding to the onset of decomposition of the materials with the elimination of water. The reactions involving weight change are complete by about 800°C.

Knowing that only 'x' Na ions of the Nazirpsios in the general formula ($Na_{(1+x)}Zr_2Si_xP_{(3-x)}O_{12}$) are displaced by hydronium ions on ion exchange, the theoretical weight loss sustained by each composition when all the water is eliminated by decomposition can be calculated. The values calculated and those obtained from TGA are given in Table 1. The observed values are higher than calculated and the extent of deviation increases with increasing x values; at x = 2 the deviation is as much as 23%. These results indicate that either more than 'x' moles of sodium ions can be displaced by hydronium ions, or that these compounds can accommodate more water molecules than that are required for H_3O^+ formation.

There are two stages in the decomposition, and these stages are very distinct in the case of hydronium zirpsios of x = 0.5 to 1.5. At x = 2.0, however, they overlap. Nevertheless, the DTG curves confirm the existence of the two stages at all four x values. Stage 1 of decomposition of compositions with x = 0.5, 1.0 and 1.5 represents respectively 25, 44 and 50% of the total weight loss. If stage 1 which is complete at about 250°C were to represent the evolution of all the water molecules associated with the protons to form hydronium ion only, then the weight loss should have been about 2/3 of the total. The fact that the weight loss is much less than the theoretical amount indicates that part of the water molecules in the hydronium ions in the hydronium zirpsios is held fast to the protons even at temperatures over 250°C. X-ray diffraction analysis of the

hydronium zirpsios heated at various temperatures (2) shows that the hydronium zirpsios retain a certain level of crystallinity even up to 400°C. According to TGA, the major part of the reaction is complete only by about 600°C; as long as protons or hydronium ions are present in the materials, the crystallinity also stays at least to some degree.

BONDING/FABRICATION OF THE HYDRONIUM ZIRPSIOS

When mixed with phosphoric acid and molded into circular discs, the composition (x value) of the hydronium zirpsio had a significant effect on the strength of the discs. The x = 0.5 and x = 1.0 compositions did not harden with the phosphoric acid. On the other hand, the samples with x = 1.5 and higher values yielded excellent dense strong discs. MOR (modulus of rupture) measured on these latter discs about 31 mm in diameter using a modified three-point method ranged between 18 and 40 MPa. No measurements could be carried out on the samples with x=0.5 and 1.0 because the disks were not rigid.

IONIC CONDUCTANCE OF THE VARIOUS PRODUCTS

Figure 3 shows a typical Admittance plot of the ionic conductivity data on a hydronium zirpsio sample for both heating and cooling cycles obtained at 50°C. It can be seen that the conductance (G_p) of the sample is significantly lower during the cooling cycle as compared to the values obtained during the heating cycle. This decrease of conductivity may be attributed to the partial loss of water from the hydronium ions when heated at 120°C.

The ionic conductivity of the hydronium zirpsio samples increases with temperature, as expected. The room temperature conductivity values for samples having x = 1.5 and 2.0 respectively are 8.2×10^{-6} and 1.4×10^{-5} $(\text{ohm-cm})^{-1}$. The corresponding values at 120°C are 1.65×10^{-4} and 1.60×10^{-4}.

Activation energies for the ion-transport processes were evaluated from the slopes of the Arrhenius plots of the data. Figures 4 and 5 represent these plots for heating and cooling cycles, respectively for x-values of 1.5 and 2.0. In the cooling cycle there is clearly an increase in activation energy. For x = 1.5, the activation energy is 7.76 kcal/mol in the heating cycle, while it is 18.0 kcal/mol in the cooling cycle. Similarly, for the x = 2.0 composition, the corresponding values are respectively, 5.9 and 17.0 kcal/mol.

Conductivity measurements made on hydronium zirpsio with x = 1.5 by the dc technique in a hydrogen atmosphere also have shown similar behaviour (3). During the heating cycle, the activation energy was 6.9 kcal/mol in the temperature range of 25 to about 100°C. On heating to 120°C the activation energy increased to 15.4 kcal/mol, and the sample maintained this higher value while cooling. The two types of measurements are thus in good agreement. The higher activation energy observed in the cooling cycle is due to the loss of water from the material which occurred when the disc was heated at 120°C. In both the proton-hopping and direct hydronium ion transport mechanisms of hydrogen ion conduction that are commonly operative in the system, the conductivity and activation energy will be related to the number of water molecules that are available for the process. The lower activation energy for the protonic conduction in the heating cycle at x = 2.0 is also due to the same reason. However, because the x = 1.5 composition is thermally more stable than the x = 2.0 composition, and because the differences in conductivities between the two are relatively small, the hydronium zirpsio with x = 1.5 will be more advantageous than at x = 2.0 when used in electrochemical devices at temperatures above 100°C.

CONCLUSIONS

Hydronium zirpsios with x value as low as 0.5 can be synthesized.

The thermal stability of hydronium zirpsios decreases with increasing x, as judged by the extent of weight loss when heated; there are two stages in the decomposition of these materials, but the mechanism involved is unclear.

The compositions with $x \geq 1.5$ can be bonded to make discs (membranes) of satisfactory strength by the phosphate technique.

Based on stability and ionic conductivity, bonded hydronium zirpsio with $x = 1.5$ appears to be the most promising.

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REFERENCES

1. Kuriakose, A.K., Wheat, T.A., Ahmad A. and Canaday, J.D., "A new method for the fabrication of polycrystalline hydrogen-conducting solid electrolytes"; Division Report ERP/MSL 85-149 (IR); CANMET, Energy, Mines and Resource Canada; 1985.

2. Kuriakose, A.K., Wheat, T.A. Ahmad, A. and Canaday, J.D. "Some properties of hydronium zirpsios"; Division Report MSL 86-29 (OP); 1986.

3. Canaday, J.D., Kuriakose, A.K., Ahmad, A. and Wheat, T.A. "Device applications of hydrogen-conducting solid electrolytes"; J. Can. Cer. Soc. 55:34; 1986.

Table 1. Calculated and observed weight losses of hydronium zirpsios of different 'x' values when calcined

'x'	% weight loss		% variation
	calculated	observed	
0.5	1.90	2.1	5.2
1.0	3.75	4.3	6.7
1.5	5.54	6.6	15.5
2.0	7.27	9.1	23.8

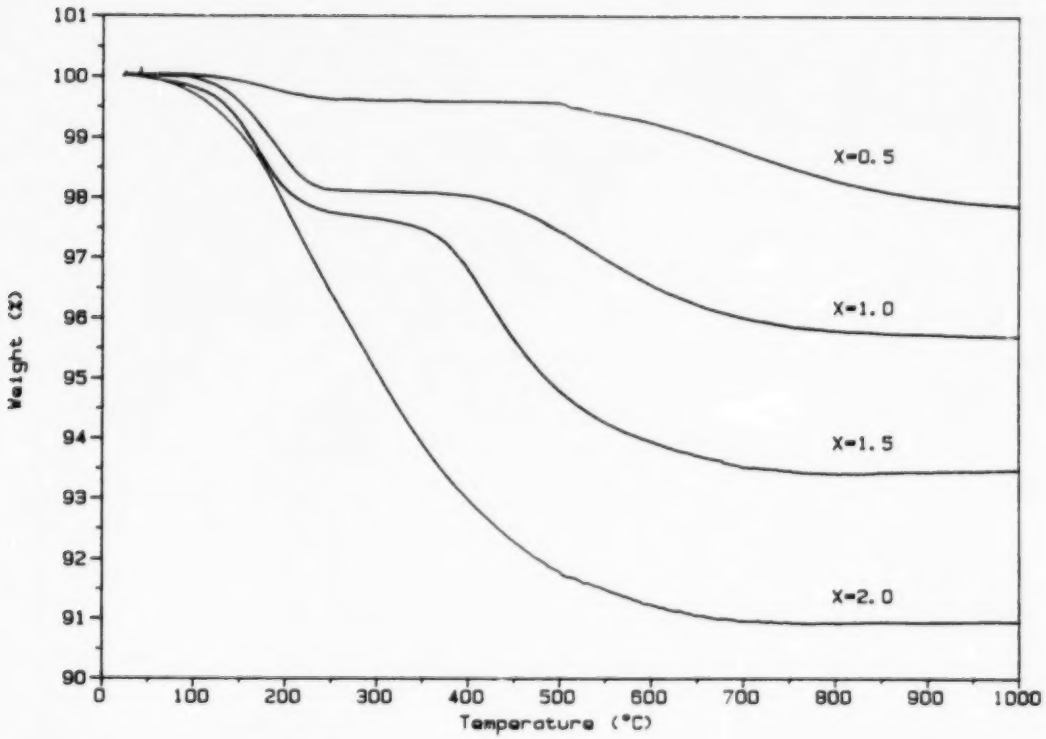

Fig. 1. TGA of hydronium zirpsios of different compositions

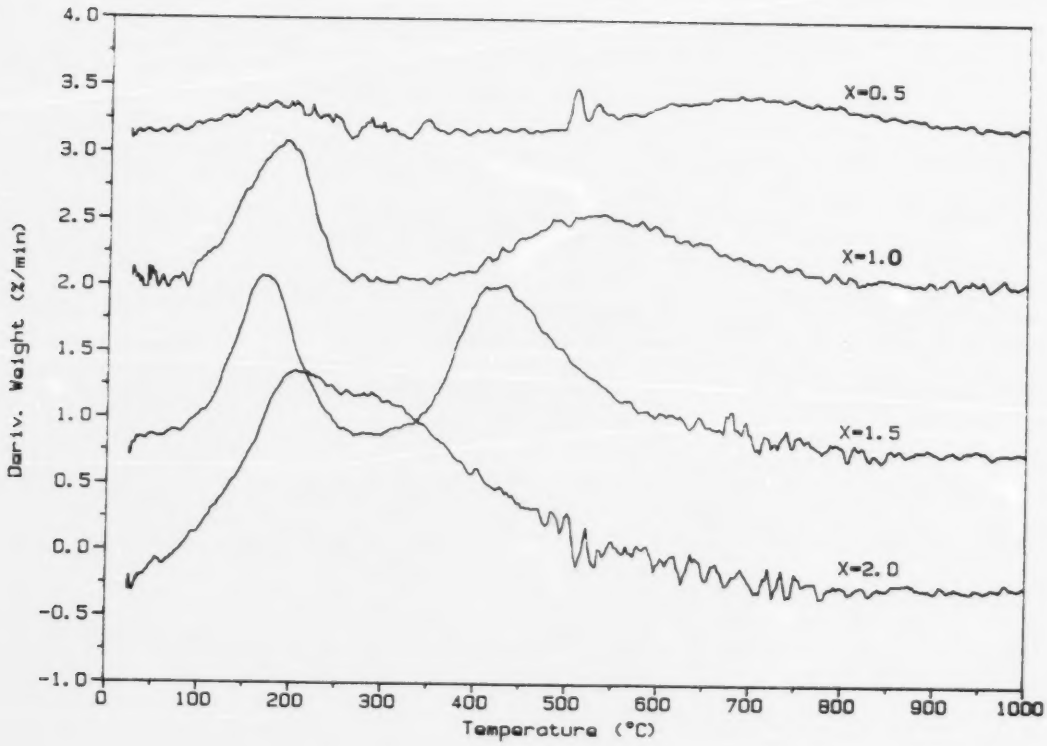

Fig. 2. DTGA of hydronium zirpsios of different compositions.

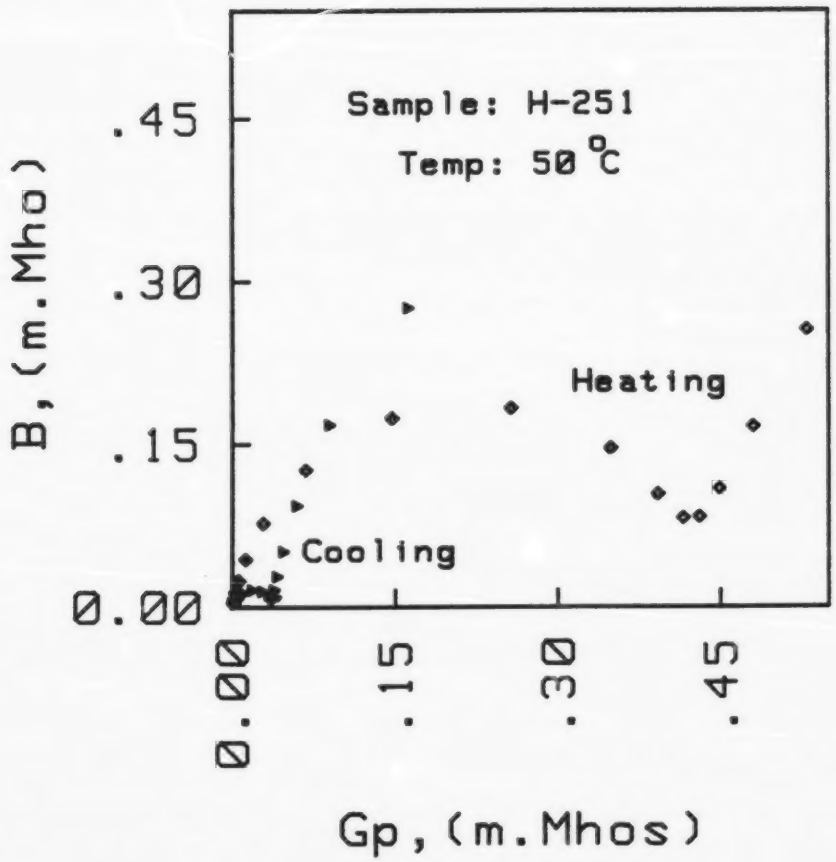

Fig. 3. Admittance plot of ac conductivity data on a hydronium zirpsio on heating and cooling cycle.

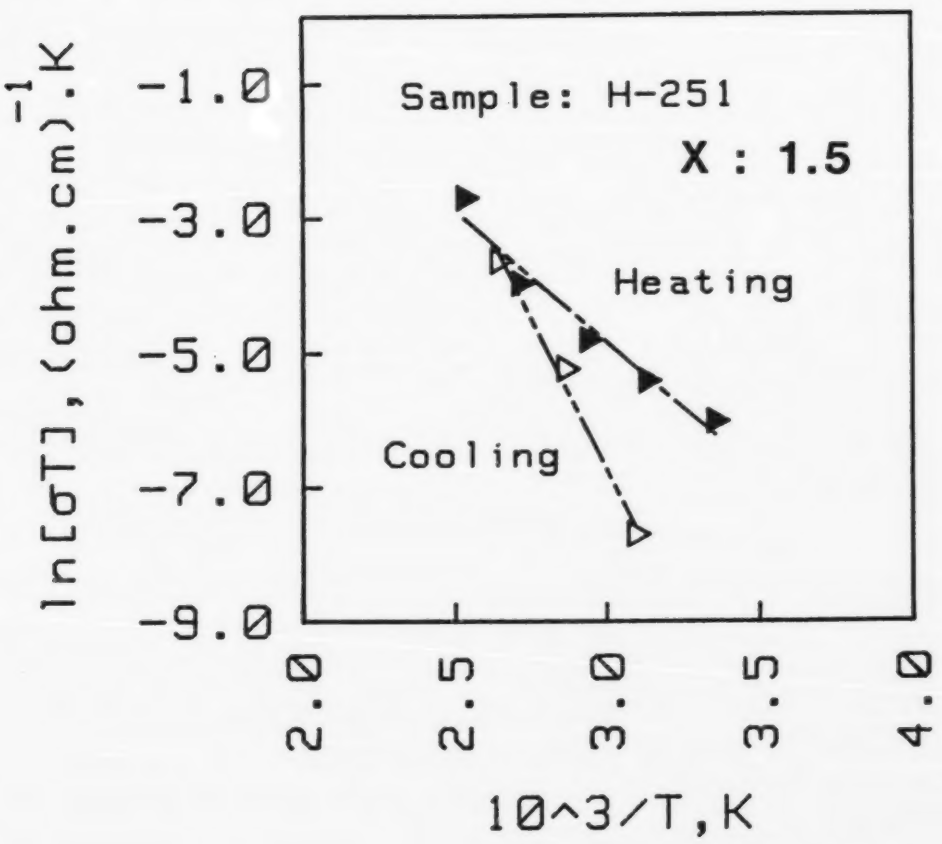

Fig. 4. Arrhenius Plots of conductivity data on hydronium zirpsios for heating and cooling cycles for x = 1.5.

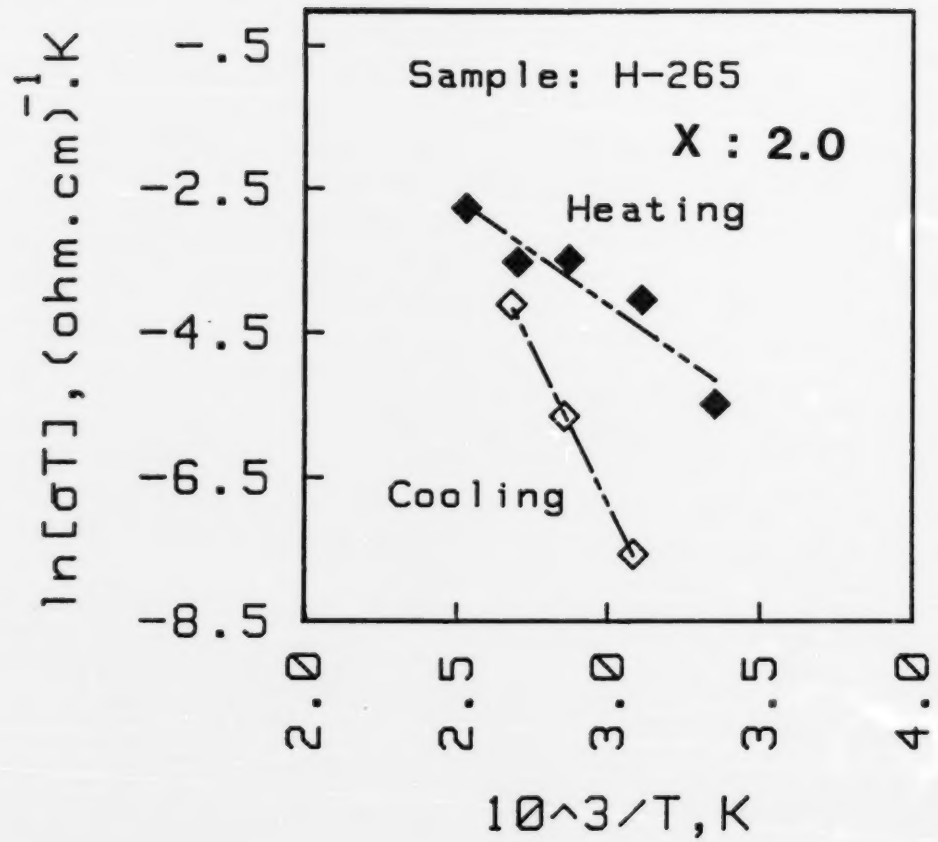

Fig. 5. Arrhenius Plots of conductivity data on hydronium zirpsios for heating and cooling cycle for x = 2.0.